

**REMARKS**

The Examiner has withdrawn her all of the indefiniteness and anticipation rejections from the previous Office Action. All claims pending in the application, namely 1-9 now stand rejected under new grounds.

Claims 1-9 have been rejected under 35 U.S.C. §103(a) as being unpatentable over EP 1086999 to Lehmann. Further Claims 5 and 6-9 stand rejected as being indefinite.

**35 U.S.C. §103(a) – Obviousness Rejection**

The pending claims 1-9 have been rejected under 35 U.S.C. §103(a) as being unpatentable over EP 1086999 to Lehmann. The Examiner maintains that this reference teaches the  $\text{SO}_2\text{CH}_3$  and the equivalence between H groups. Applicants respectfully disagree.

The general formulas (V) and (VI) of the invention dyes as defined in Claim 1 are similar. The main difference between the two formulas is the position of the azo group in the naphthyl moiety. In dyes of general formula (V), the azo group is in position  $\beta$  of the naphthyl moiety. In dyes of general formula (VI), the azo group is in position  $\alpha$  of the naphthyl moiety.

A further difference is the presence or the absence of the substituent  $\text{R}_4$ .  $\text{R}_4$  may represent hydrogen,  $\text{SO}_3\text{M}$ ,  $\text{NH}_2$  or  $\text{NHSO}_2\text{D}_3$ , where  $\text{D}_3$  represents alkyl having from 1 to 6 C atoms, phenyl or substituted phenyl where the substituents are selected from the group consisting of methyl, fluoro, chloro or bromo.

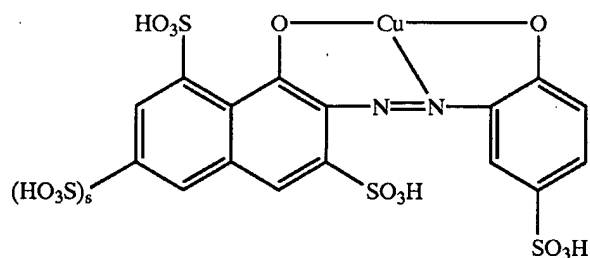
The naphthyl part of the invention dyes of formula (V), in the case where  $\text{R}_4$  represents  $\text{SO}_3\text{M}$ , corresponds therefore to Lehmann's dyes where s is equal to 1.

The naphthyl part of the invention dyes of formula (V), in the case where  $\text{R}_4$  represents hydrogen, corresponds therefore to Lehmann's dyes where s is equal to 0.

**The dyes of general formula (VI) have no equivalents in EP 1,086,999 or US 6,521,032. Therefore the Examiner's obviousness rejections are considered to be directed only against dyes of general formula (V).**

The Examiner alleges that the following pair of dyes of EP 1,086,999 (or of the equivalent patent US 6,521,032) teaches the  $\text{SO}_2\text{CH}_3$  and the equivalence between H groups:

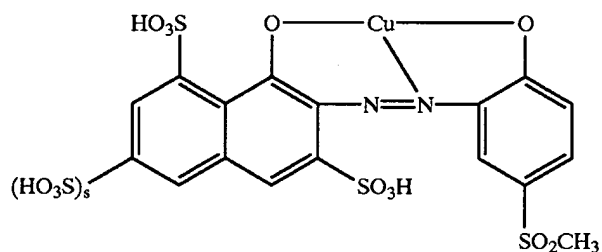
4/5



dye 4/5 of US 6,521,032

together with

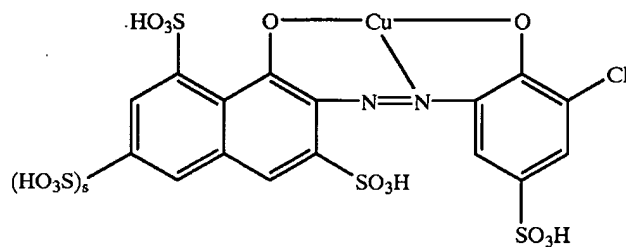
18/19



dye 18/19 of US 6,521,032

and

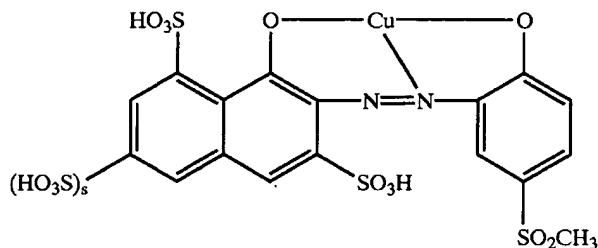
10/11



dye 10/11 of US 6,521,032

together with

18/19



dye 18/19 of US 6,521,032

Dye 18/19 of Lehmann contains a  $\text{SO}_2\text{CH}_3$  in the position opposite to the hydroxy substituent on the right side of the molecule. This is a substituent also claimed in our dyes (R1 represents alkyl). The other Lehmann dyes 4/5 and 10/11 contain a  $\text{SO}_3\text{H}$  substituent in this position. The  $\text{SO}_3\text{H}$  substituent is obtained from the  $\text{SO}_2\text{CH}_3$  substituent when the alkyl group is replaced by a **hydroxy** group and is **not** hydrogen, as the Examiner alleges.

The dyes according to the invention contain a  $\text{SO}_3\text{H}$  substituent in the ortho position to the copper complexing hydroxy group. US 6,521,032 to Lehmann mentions that the phenyl group may be substituted by a substituent R which is  $\text{C}_1 - \text{C}_4$  alkyl,  $\text{C}_1 - \text{C}_4$  alkoxy or halogen (page 2, column 2, line 15). There is no suggestion at all that a  $\text{SO}_3\text{H}$  substituent could be introduced. Furthermore, it is not suggested that the substituent should be in the ortho position to the hydroxy substituent.

The invention examples show that the introduction of the  $\text{SO}_3\text{H}$  substituent in the ortho position to the copper complexing hydroxy group results in dyes having superior properties regarding the stability in contact with ambient air. Comparative dye (I) in Tables 3 - 6 is in fact dye 18/19 of US 6,521,032.

Tables 3 - 6 contained in the specification have been modified below, having removed the data of comparative examples II, III and IV which are not relevant to this response. In sum, the tables illustrate optical density before and after storage and lists the density difference in % for Dyes 10 and 13 which are invention dyes of general

formula (V); dye 102 which is an invention dye of general formula (VI); and dye (I) which is dye 18/19 of U.S. 6,521,032 to Lehmann.

**Table 3**

Dye	Optical Density before Storage	Optical Density after Storage	Density Difference in Percent
13	1.64	1.43	<b>12.8</b>
10	1.66	1.45	<b>12.7</b>
102	1.72	1.46	<b>7.0</b>
I	1.81	1.56	13.8

**Table 4**

Dye	Optical Density before Storage	Optical Density after Storage	Density Difference in Percent
13	0.59	0.55	<b>6.8</b>
10	0.59	0.54	<b>8.5</b>
102	0.59	0.56	<b>5.1</b>
I	0.68	0.58	14.7

**Table 5**

Dye	Optical Density before Storage	Optical Density after Storage	Density Difference in Percent
13	1.57	1.37	<b>12.7</b>
10	1.64	1.43	<b>12.8</b>
102	1.53	1.43	<b>6.5</b>
I	1.75	1.48	15.4

**Table 6**

Dye	Optical Density before Storage	Optical Density after Storage	Density Difference in Percent
13	0.59	0.53	<b>10.2</b>
10	0.58	0.52	<b>10.3</b>
102	0.61	0.58	<b>4.9</b>
I	0.67	0.57	14.9

These results show that the invention dyes 10 and 13 (formula V) and especially invention dye 102 (formula VI) show a better stability in contaminated ambient air than comparative dye I (dye 18/19 of US 6,521,032).

It is well-settled that the mere fact that the prior art could be modified to form the invention would not make that modification obvious unless the prior art suggested the desirability of the modification. In re Laskowski, 10 U.S.P.Q. 2d 1397, 1398 (Fed. Cir. 1989); In re Gordon, 733 F.2d 900, 902, 221 U.S.P.Q. 1125, 1127 (Fed Cir. 1984).

There is no teaching or suggestion in the Lehman reference as to the  $\text{SO}_2\text{CH}_3$  and the equivalence between H groups. Accordingly, Applicants assert that one skilled in the art would not find it obvious to make the modification the Examiner suggests to obtain the compounds of the present invention. Applicants believe they have overcome the obviousness rejection of claims 1-9 which should now be withdrawn.

### **35 U.S.C. §112 Rejections**

Claim 5 has been rejected under 35 U.S.C. 112, second paragraph, as being indefinite for failing to particularly point out and distinctly claim the subject matter of the invention. The Examiner states that the claims indicate "coppering agents" without specifying which compounds they mean and further that there is no specific definition of these agents. Applicants respectfully disagree.

Applicants assert that the term "coppering compound" is well known to someone skilled in the art of making dyes, in particular metallized dyes. Applicants enclose a copy of the relevant pages 299 and 302-305 from an article entitled "Metal-Complex Dyes" found in "Ullmann's Encyclopedia of Industrial Chemistry", Fifth, completely revised edition, Volume A16, VCH Verlagsgesellschaft mbH, Weinheim, Germany, ISBN 3-527-20116-5, (1990). This chapter starts (at page 302, 2<sup>nd</sup> column) as follows:

"The chief synthetic methods for metal complexes are summarized in Table 1. Most 1: 1 nickel and copper complexes are prepared from the corresponding salts at pH 4 – 7 in the presence of bases such as sodium acetate and ammonia between 25 and 70° C."

Table 1 specifically lists copper sulfate  $\text{CuSO}_4$  as a copper salt.

Applicants also enclose the relevant pages 216-219 from "Colorants and auxiliaries", Volume 1 – Colorants, Society of Dyers and Colourists, Bradford, ISBN 0-901-95651-1 (1990). Page 218, lines 13 – 16 states:

"Once the mono- or dis-azo chromophore is obtained, metallisation can be achieved with cuprammonium sulphate in the presence of an alkanolamine such as diethanolamine."

Accordingly, Applicants believe Examiner's indefiniteness rejection of Claim 5 has been overcome and should be withdrawn.

Claim 6 has also been rejected under 35 U.S.C. 112, second paragraph, as being indefinite for failing to particularly point out and distinctly claim the subject matter of the invention. The Examiner states that the claim recites a process without specifying the steps involved in the process.

Claim 6 has been amended to clarify a process for recording text and images on materials selected from the group consisting of natural or synthetic fiber materials, nanoporous materials, leather and aluminum by applying thereto, with an ink jet printer, a compound of formulas (V) and (VI).

New Claim 10 has been added to define a process for dyeing and printing the same materials as in Claim 6.

These new claims are fully supported by the specification at page 9, lines 19-23 and 24-28; and Example 2 page 12 lines 20-26. No new matter has been added by these amendments. Accordingly, the Examiner's indefiniteness rejection of Claim 6 has been overcome and should be withdrawn.

Finally, the Examiner has rejected Claims 7-9 as being indefinite stating that the inks and liquid dyes are compositions and should be rewritten in "ink composition" format. Applicant respectfully disagrees.

Claim 9 has been amended to change dependency from being an independent claim to being a dependent claim, dependent on Claim 8.

A liquid dye preparation as defined in Claim 7 is not the same as an ink, defined in Claims 8 and 9. A liquid dye preparation is obtained for example by dissolving a dye in a suitable solvent (see Applicant's specification at page 10, lines 3 - 5). A liquid dye

preparation may also be obtained for example by desalting of the reaction solution after dye coupling (see Applicant's specification at page 10, lines 6 - 9).

An ink for ink jet printing contains, in addition to the dyes, other compounds (see example 2) such as water, glycerol, propylene glycol, surfactants and biocides.

Accordingly, Applicants believe that Claims 7-9 as written are proper and are not indefinite.

In view of the above arguments, the Applicants believe they have overcome both the anticipation and indefiniteness rejections. Applicants submit that this application is now in condition for allowance. Applicants hereby request reconsideration of this application and allowance of pending claims 1-10. If a telephone interview would be useful to advance this case, then the Examiner is invited to telephone the undersigned.

Respectfully submitted,  
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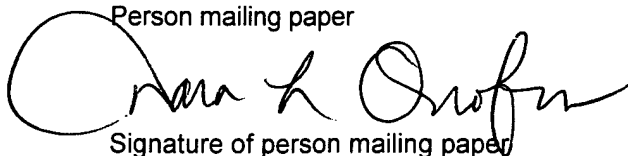
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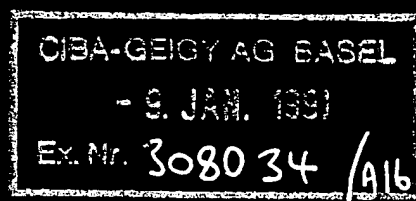
# Ullmann's Encyclopedia of Industrial Chemistry

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Volume A 16:

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Editors: Barbara Elvers, Stephen Hawkins, Gail Schulz





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# Metal-Complex Dyes

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WINFRIED MENNICKE, Bayer AG, Leverkusen, Federal Republic of Germany (Chap. 6)

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## 1. Introduction and History

The use of metal complexes as dyes has its origins in *mordant dyeing*, a process that can be traced back to the Middle Ages. In mordant dyeing, textile dyes or the dyed fabrics themselves are treated with specific metal salts, which leads to both a bathochromic shift in color and a distinct dullness. Resistance to the effect of light or washing is also greatly improved. Metal compounds commonly employed earlier include aluminum, chromium, and iron salts.

Important events in the historical development of metal-complex dyes can be summarized as follows [5], [12]:

- 1887 Synthesis of the first metallizable azo dye, alizarin yellow, from diazotized 4-nitroaniline and salicylic acid (R. NIETZKI)
- 1891 Formulation of the theory of coordination (A. WERNER)

- 1893 Synthesis of the first metallizable 2,2'-dihydroxyazo dye (E. BERGMANN and O. BORGMANN)
- 1908 Elucidation of the stereochemistry of metal complexes (A. WERNER)
- 1912 Synthesis of the first premetallized 1:1 chromium complex (R. BOHN, BASF)
- 1915 Patenting of a strong-acid dyeing process for 1:1 chromium complexes (Ciba)
- 1920 Marketing of 1:1 chromium complexes: the Neolan series (Ciba) and the Palatin Fast series (BASF)
- 1927 First synthesis of copper phthalocyanine (H. DE DIESBACH and E. VON DER WEID)
- 1949 Development of the first 1:2 chromium complexes lacking sulfo groups: Irgalan dyes (G. SCHETTY, Geigy)
- 1954 Marketing of Neopalatin dyes (BASF)
- 1962 Introduction of Lanacron dyes as homogeneous 1:2 chromium complexes containing a sulfo group (Ciba)
- 1970 Acidol M dyes (BASF) sold as 1:2 chromium complexes with two sulfo groups

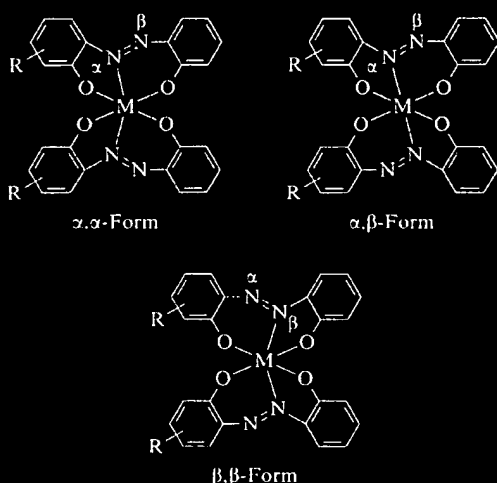


Figure 4. N- $\alpha,\beta$ -Isomers of 1:2 metal complexes  
M =  $\text{Co}^{3+}$ ,  $\text{Cr}^{3+}$

tra and solubilities differ. In solution, each of the isomers undergoes equilibration to regenerate the original mixture. Once again, the proposed structure of one of these isomers has been confirmed by X-ray structural analysis [22].

With asymmetric 1:1 and 1:2 metal complexes a second type of isomerism becomes possible because different nitrogen atoms from the tricyclic ligands can be bound to the central atom in different ways. Two isomers may be distinguished in a 1:1 complex [23] and three in a 1:2 complex (Fig. 4) [24]. These isomers have been detected by NMR spectroscopy [25].

Such N- $\alpha,\beta$ -isomerism is precluded in complexes of the 1:1 and 1:2 types if the third position ortho to the azo function is occupied by methyl or methylene groups [26]. Thin layer chromatographic separation of N- $\alpha,\beta$ -isomers has been described [27].

The third type of isomerism is found in 1:2 complexes with 5/6-membered rings and is attributed to the tautomeric hydrazone structures of the azo ligands, in which an  $sp^3$ -hybridized nitrogen atom serves as the electron donor. Three conformationally distinct complexes arise [28]. A thorough study of this situation utilizing modern spectroscopic methods is reported in [29]. Figure 5 illustrates the tautomers containing only one 1-hydroxyl group, which can be used to synthesize cobalt complexes.

The fact that numerous isomeric complexes coexist in equilibrium means that the resulting colors tend to be rather dull. In contrast, planar dyes such as the copper phthalocyanines and copper formazans are brilliant in color.

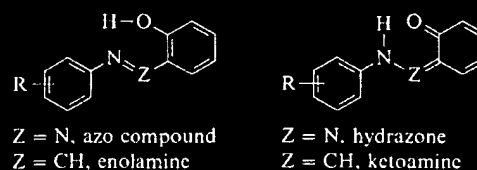


Figure 5. Tautomerism in azo and azomethine compounds

### 3. Production

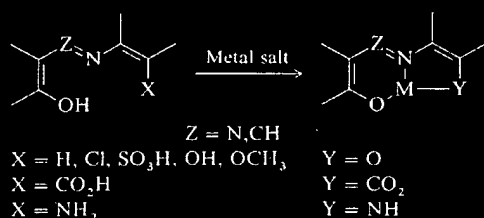
The chief synthetic methods for metal complexes are summarized in Table 1. Most 1:1 nickel and copper complexes are prepared from the corresponding salts at pH 4–7 in the presence of bases such as sodium acetate and ammonia between 25 and 70 °C. *Dealkylative coppering* is the method of choice for water-soluble polyazo compounds. This may involve initial formation of a 1:1 copper complex in which the ether group is already coordinated to copper. Reaction is carried out in the presence of buffers such as sodium acetate, alkanolamines, or pyridine at elevated temperature (> 80 °C). Nucleophilic substitution is facilitated by the neighboring azo group, and if X = H (Table 1), simultaneous oxidation is required (*oxidative coppering* [30]). Oxidative degradation of the original dye is a danger in this reaction, so very mild conditions are required. The 2,2'-dihydroxy copper complexes are formed from the corresponding 2-halogen compounds in strongly alkaline medium [31]. 2-Sulfonic acids are also susceptible to nucleophilic exchange.

Dealkylative and oxidative coppering represent technical processes, because few direct methods are known for preparing azo metal complexes with 2-hydroxy substituents on both sides of the azo group. This is a consequence of the limited availability of 2-aminophenols and the difficulty of coupling the corresponding diazonium salts (2-quinone diazides). Copper complexes prepared in this way can subsequently be converted to metal-free dyes and then to the corresponding chromium complexes [32].

Iron complexes are prepared under weakly acidic conditions at slightly elevated temperature (40–80 °C).

The 1:1 cobalt(III) complexes cannot be prepared in acidic solution. Nevertheless, the greater stability of cobalt(III) amine complexes [9], [33] can be exploited to obtain 1:1 cobalt complexes with three  $\text{NH}_3$  ligands [34] or the

Table 1. Synthetic methods for metal complexes



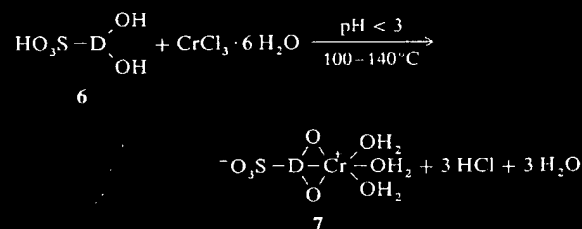
Reagents	X	pH	Temperature, °C
<i>Cu-Ni 1:1 complexes</i>			
CuSO <sub>4</sub> , NH <sub>3</sub> , CH <sub>3</sub> COONa	OH, CO <sub>2</sub> H	4-6.5	25-70
CuSO <sub>4</sub> , NH <sub>3</sub> /H <sub>2</sub> NCH <sub>2</sub> CH <sub>2</sub> OH	OCH <sub>3</sub>	> 7	> 80
CuSO <sub>4</sub> , CH <sub>3</sub> COONa/H <sub>2</sub> O <sub>2</sub>	H	4.5-8	25-50
<i>Fe 1:2 complexes</i>			
FeSO <sub>4</sub> , CH <sub>3</sub> COONa	OH	5	40-80
<i>Co 1:1, 1:2 complexes</i>			
CoCl <sub>2</sub> , NaOH, air	OH	5-8	40-80
CoCl <sub>2</sub> , NaOH, H <sub>2</sub> O <sub>2</sub>	OH	5-6	40-70
CoCl <sub>2</sub> , NH <sub>3</sub> , glycols	OCH <sub>3</sub>	> 7	80-120
<i>Cr 1:1 complexes</i>			
Cr <sup>3+</sup> salt, acid, H <sub>2</sub> O, or glycols	OH, CO <sub>2</sub> H NH <sub>2</sub> , OCH <sub>3</sub>	< 3	100-140
<i>Cr 1:2 complexes</i>			
Cr <sup>3+</sup> salt, NaOH	OH, CO <sub>2</sub> H, NH <sub>2</sub>	4-8	80-100
Cr <sup>3+</sup> salt, tartaric acid, salicylic acid, NaOH		7-9	80-100
Na <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> , glucose, NaOH		7-9	80-100
Cr <sup>3+</sup> salt, amides, glycols		7-9	100-140
Na <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> , glycols, NaOH	OCH <sub>3</sub>	> 7	100-130

even more stable complexes with ethylenediamine, triethylenediamine, or phenanthroline [35]. Nitrite as a strong nucleophile also produces stable complexes [36].

The metal ion in 1:2 cobalt complexes is also trivalent, but such dyes are manufactured from the more stable cobalt(II) salts. Atmospheric oxygen serves as the oxidant, and reaction conditions are very mild: 40–80°C and near-neutral pH. If cobaltization proceeds slowly, the metal-free dye may suffer degradation because it can act as an oxidant. The result is a decrease in yield, but important characteristics of the dye may also be adversely affected. The usual remedy is dropwise addition of dilute hydrogen peroxide along with the cobalt(II) chloride solution. Demethylative cobaltization requires temperatures > 100°C, achieved by carrying out the reaction in high-boiling glycols. Base (e.g., ammonia, alkanolamines, or sodium hydroxide) must also be added.

The 1:1 chromium complexes containing sulfonic acid groups are prepared below pH 3 at

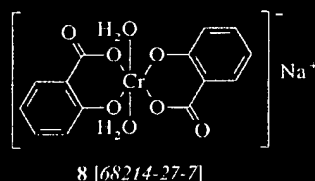
100°C (disulfo derivatives) and up to 140°C (monosulfonated compounds). A reaction temperature > 100°C is achieved either in water under pressure or in glycols. The 1:1 chromium dyes are isolated from acidic solutions as their slightly soluble betaines (7) [5].



D = azo or azomethine residuc

Irrespective of the number of sulfo groups, temperatures  $> 100^{\circ}\text{C}$  are always required in the demethylative incorporation of chromium. The usual source of chromium is chromium(III) oxide (obtained as a byproduct of dichromate oxidation), which is first dissolved in hydrochloric, sulfuric, or formic acid.

Preparation of 1:2 chromium complexes generally requires higher reaction temperatures than the corresponding 1:2 cobalt compounds because the hexa-aquo chromium ion present in solution is very stable. This subject has been discussed in [9]. Chromium incorporation is usually conducted in near-neutral solution but can be accelerated by the addition of base. An anionic precomplex with tartaric, oxalic, or salicylic acid is used to prevent the precipitation of chromium hydroxide [37]. The 1:2 chromium complex with salicylic acid (8) is particularly effective.



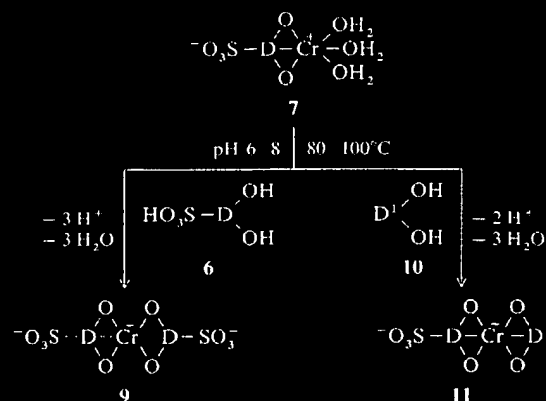
An alternative method of preparing 1:2 chromium complexes under milder aqueous conditions is based on the use of an alkaline dichromate-glucose solution, in which a very reactive chromium(III) accessory complex forms as an intermediate [38]. The process is most important in the synthesis of 1:2 chromium complexes containing sulfonamide groups. Special precautions are necessary because of the toxicological risk of handling solid dichromate.

The introduction of alcohols [39] and carboxamides [40] as solvents for azo dyes that are only slightly soluble in water represented a technical advance. Formamide is particularly important because it promotes formation of 1:2 chromium complexes by buffering the acid that is released. The slightly soluble complexes are isolated by dilution with water.

Introduction of chromium by demethylation requires the use of sodium dichromate in glycol, which serves as both a high-boiling solvent and a reductant.

Two routes are used for preparing 1:2 metal complexes: the addition method and mixed metallization. The addition method leads first to a 1:1 chromium complex (7), which is isolated and subsequently reacted with the metal-free dye 6 to give the symmetric 1:2 complex 9. Use in the second step of a dye with a different structure (10) but still capable of forming complexes, provides a route to uniform asymmetric 1:2 complexes (11).

For economic reasons, large-scale synthesis of symmetric 1:2 complexes is usually carried

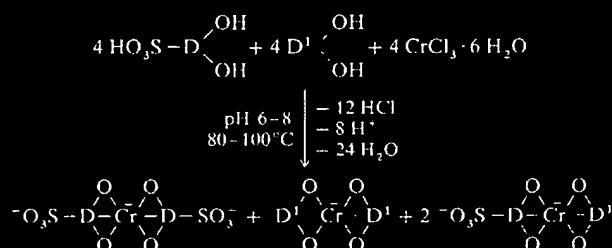


D, D' = azo or azomethine residue

out without isolation of the intermediate, but synthesis of asymmetric 1:2 complexes (e.g., those with only a single sulfonic acid group) is necessarily a stepwise process.

Mixed metallization is particularly important in the synthesis of 1:2 cobalt complexes because of the inaccessibility of the corresponding 1:1 materials [41].

Two equivalents of an azo or azomethine dye are reacted with one equivalent each of a Cr(III) or a Co(II) salt to give a single symmetric 1:2 metal complex. If the reaction is conducted with two different dyes, both capable of forming complexes, a statistical mixture of 1:2 metal complexes arises, i.e., two symmetric complexes and one asymmetric complex:



D, D' = azo or azomethine residue

All three of the resulting dyes can be detected chromatographically. The solubility of such a mixture is often higher than that of a mechanically prepared mixture of the same dyes. Mixed metallization opens the way to a large number of potential combinations, permitting the manufacture of brown, olive, marine blue, and black color tones that are otherwise difficult to achieve.

Use of three diazo and three coupling components can result in up to nine metal-free azo

dyes, and these in turn can lead to 45 different 1:2 metal complexes. If one begins with ten components the number of possibilities increases to more than 5000.

#### 4. Ecology and Toxicology

Dyes may enter the environment at several points: during production, in the dye works, and during use of the finished goods [42]. Losses during production and use depend on molecular structure, but average values from the textile, leather, and paper industries appear to be about 10% of the total annual production of 450 000 t [43].

The effectiveness of a dye is a function of its stability with respect to a wide range of chemical and physical influences. Thus, dyes are degraded only slightly during normal wastewater treatment due to short residence times and aerobic conditions. Nevertheless, between 40 and 80% of the material is adsorbed onto the activated sludge. Further degradation in the sediment by reductive anaerobic processes is rapid.

Toxicity studies in fish, involving more than 3000 commercial dyes, revealed that seven metal complexes had an  $LC_{50} \leq 1$  mg/L. Such concentrations are not present in colorless effluents leaving a wastewater treatment plant (dye concentrations  $\geq 1$  mg/L are clearly visible). Typical distribution coefficients  $P$  of the complexes in *n*-octanol–water allow their bioaccumulation in fish to be estimated. Values indicate that the dyes are not bioaccumulated because solubilities in water are either too high or too low [44]. Studies also indicate that toxicity to algae and inhibitory effects on clarified sludge bacteria are negligible [45]. Metal-complex dyes possess only slight acute toxicity [46]. A published list of dyes classified as toxic ( $LD_{50} \leq 200$  mg/kg) does not include metal complexes; their  $LD_{50}$  values all exceed 2000 mg/kg. Proposals for the safer handling of dyes are described in [47]. Relevant international regulations are reviewed in [48].

Economic and technological factors, together with ecologically suspect dyeing practices (e.g., large amounts of heavy metals in mordant baths), preclude the use of natural dyes as an alternative to synthetic substances [49]. Heavy-metal residues (including chromium) in effluents from dye production pose a risk of water pollution, but they can be eliminated by precipitation

with calcium salts [50]. Processes for removing residual heavy metals from the reaction mixture in the form of water-soluble complex dyes are described in [51].

Different problems are posed by the after chroming process in which a metal-free complexable dye is used to stain wool in a process similar to application of an acid leveling dye. The dye is then converted into a metal-complex dye directly on the fibers with the aid of sodium dichromate. Improved procedures have drastically reduced the concentration of chromium salts in the corresponding effluents [52]. A report on the cleaning of effluents from textile mills is presented in [53].

#### 5. Uses of Metal-Complex Dyes

Metal-complex dyes are unsurpassed in terms of range of application. Apart from certain restrictions affecting a few synthetic fibers, virtually all substrates can be dyed or printed with these substances but with dull shades. No other class of dyes provides such a generally high level of fastness, particularly lightfastness. Countless shades from greenish yellow to uniform black can be obtained by using different metals and combining different metal-complex dyes.

##### 5.1. Textile Dyeing

###### 5.1.1. Wool and Polyamides

(→Azo Dyes, A3, pp. 272–274)

Worldwide wool production is currently about  $1.6 \times 10^6$  t, with a very low growth rate. Wool constitutes only about 4% of all textile fibers, but because deep shades such as blue, brown, and black dominate, the corresponding fraction of total dye consumption is twice as great, namely 8%. Technical and economic criteria for selecting wool dyes are discussed in [54].

Premetallized complex dyes constitute 30% of all wool dyes, a proportion slightly less than that assigned to secondary chromium incorporation dyes [52]. These mordant dyes are still important, especially for dyeing wool in dark shades with very high fastness. Premetallized dyes are 1:1 chromium, 1:2 chromium, or 1:2 cobalt complexes (no other metals are used). Their anionic character is responsible for their great colorfastness with respect to the highly

# Colorants and auxiliaries

Organic chemistry and application properties

Volume 1 – Colorants

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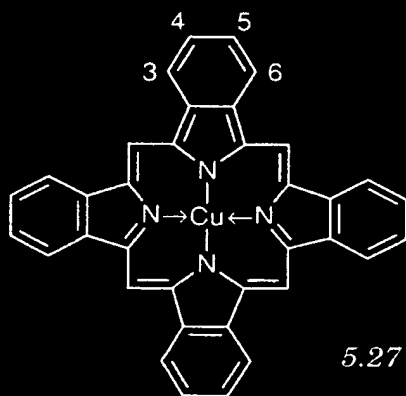


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the outermost 3-, 4-, 5- and 6-positions in each aromatic or quinonoid ring, so that the colour range anticipated from the presence of auxochromes is extremely limited.

## 5.5 PREPARATION OF METAL COMPLEXES

There are numerous ways of introducing a metal atom into a dye molecule to form a metal complex. Most attention has been paid to chromium and cobalt for this purpose; there are essential differences in the preparation conditions of their complexes.

### 5.5.1 Chromium complexes

Table 5.1 (in section 5.3.1) shows that the trivalent hexa-aquo chromium ion possesses three low-energy  $t_{2g}$  orbitals, each singly occupied. The ligand field stabilisation energy is considerable as a consequence. Since this energy has to be overcome, the replacement of the water ligand groups by other entities is a slow process, and the most successful practical methods are designed to take this into account.

The replacement reactions may be represented generally by a two-stage process (Schemes 5.4 and 5.5, in which  $D^{2-}$  represents a tridentate azo dye system, assuming prior ionisation). The reaction in Scheme 5.4 is slower than that in Scheme 5.5 and is the rate-controlling step. Where a tridentate *o,o'*-dihydroxyazo dye is used in excess with a hydrated chromium salt under conditions favouring 1:2 metal-dye complex production, no 1:1 complex is formed, indicating that the reaction in Scheme 5.5 is more rapid than that in Scheme 5.4. In order to obtain a 1:1 complex, therefore, it is necessary first to obtain the 1:2 complex (favoured at  $\text{pH} > 9$ ) and then to treat this complex under strongly acid conditions; the reaction in Scheme 5.5 then proceeds to the left.



Scheme 5.4

*Scheme 5.5*

The chromium salt used can be the acetate, chloride or sulphate, the reaction with metallisable dyes being carried out in aqueous media at the boil at atmospheric pressure or greater. Where the metallisable dye is insoluble in water a solvent such as ethanol or ethylene glycol may be added.

Other solvents such as formamide or molten urea have been recommended and it is probable that such solvents will displace water molecules and coordinate with the chromium(III) ion as the first step in the reaction. By using organic chelates of chromium, such as those derived from oxalic or tartaric acid, in place of or in addition to hydrated chromium(III) salts, the difficulty of replacing the strongly coordinated water molecules in the first stage of reaction is removed and the reaction can be carried out at high pH without the precipitation of contaminating chromium hydroxide. The use of the complex ammonium chromisalicylate (5.7) in this connection should be noted.

### 5.5.2 Cobalt complexes

Like trivalent chromium, trivalent cobalt complexes contain three low-energy  $t_{2g}$  orbitals, this time each doubly occupied. In general trivalent cobalt complexes are easier to prepare than the chromium analogues, although their properties are similar. Direct use of cobalt(III) salts is avoided since the  $\text{Co}^{3+}$  ion is strongly oxidising and slow to react. Most 1:2 metal-dye complexes are prepared by the reaction between the metallisable dye and a cobalt(II) salt at a relatively high pH. The product is invariably the diamagnetic cobalt(III) complex, the oxidation of the cobalt(II) ion taking place through reduction of some azo dye molecules. This can be avoided by adding a less stable oxidising agent. Unlike the corresponding 1:1 chromium complexes, 1:1 cobalt-dye complexes are unstable and cannot be obtained in acceptable yield at low pH. However, advantage can be taken [25] of the strong affinity of nitrogen electron donors for cobalt. The reaction of the cobalt(II) ion with a tridentate dye molecule in an excess of ammonia yields a 1:1 complex in which the coordination sphere is completed by three ammonia molecules. This again is diamagnetic, indicating the absence of unpaired electrons necessary to achieve an  $sp^3d^2$  octahedral structure.

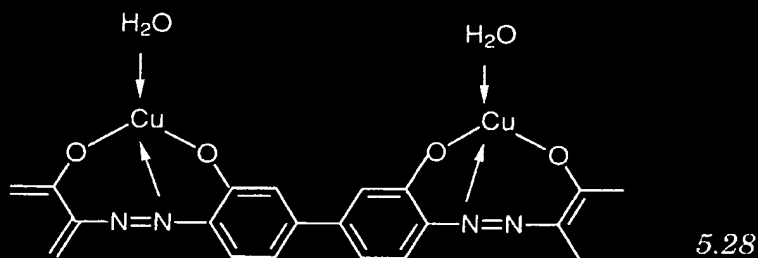
Although 1:1 metal-dye complexes have little importance in direct application to textile substrates, they are widely used as intermediates in the production of unsymmetrical 1:2 metal-dye complexes, particularly when the asymmetry arises from the presence of one or more sulphonic acid

groups in one of the metallisable dye ligands partaking in complex formation.

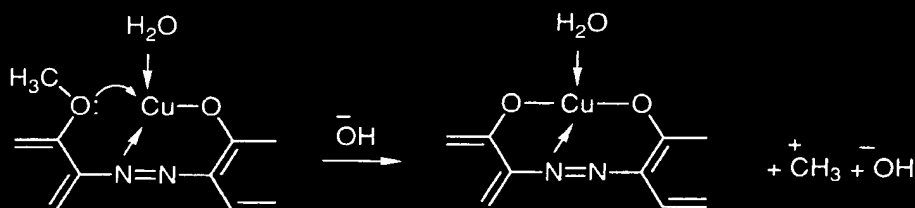
### 5.5.3 Copper complexes

The only copper complexes of tridentate azo compounds are 1:1 complexes, since copper has a CN of 4; they are little used on wool or nylon. They can be prepared by the reaction of the azo compound with a copper salt in an aqueous medium at 60°C.

The major application for copper complexes is in the prior metallisation or aftertreatment of direct dyes containing at least one *o,o'*-dihydroxyazo or *o*-methoxy-*o'*-hydroxyazo chromophore system. In the manufacture of these dyes it is sometimes easier to synthesise the latter system simply because the *o*-methoxyarylamines when diazotised are more efficient couplers than are the corresponding *o*-hydroxyarylamines. Once the mono- or dis-azo chromophore is obtained, metallisation can be achieved with cuprammonium sulphate in the presence of an alkanolamine such as diethanolamine. The best-known example is the disazo dye C.I. Direct Blue 1, the greener copper complex of which contains the system shown in structure 5.28.



During metallisation the two methoxy groups originating in the central tetrazotised dianisidine component are demethylated. It is probable that coordination occurs between the copper(I) ion and the electron-rich oxygen of the methoxy group with simultaneous or subsequent loss of the methyl group as a carbonium ion, according to Scheme 5.6. The removal of the methyl group is probably assisted by the coordination of the methoxy oxygen, particularly in the presence of electronegative groups in *p*-positions.



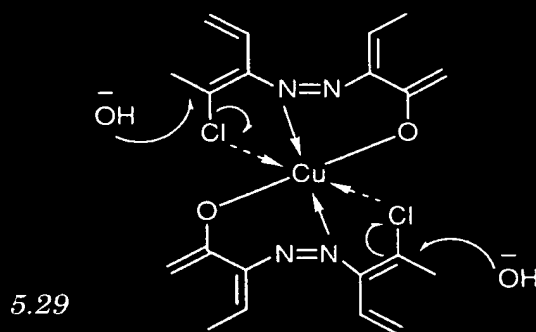
Scheme 5.6

### *Oxidative coppering*

Other methods of introducing copper into dye structures include the process of oxidative coppering. In this method an azo compound containing a single *o*-hydroxy group is treated with a copper salt and an oxidant in an aqueous medium at 40–70°C and pH 4.5–7.0. Pfitzner and Baumann [26] have reviewed applications of this method. Sodium peroxide, sodium perborate, hydrogen peroxide or other salts of peroxy acids may be used as oxidants, the function of which is to introduce a second hydroxy group in the *o*'-position. The situation is similar to that investigated earlier by Morgan and Main-Smith, who found that C.I. Acid Red 14, containing a single *o*-hydroxyazo grouping, did not form a chromium complex with chromium salts but could do so on oxidation with chromic acid. The resultant complex was later found to be identical with that obtained by treating C.I. Mordant Black 3 with chromium salts. The latter dye differs from C.I. Acid Red 14 only in the presence of a second *o*'-hydroxy group.

### *Replacement of labile halogen*

The halogen atom in an *o*-halogeno-*o*'-hydroxyazo compound may be replaced by a hydroxy group under mild conditions provided that the halogen atom is activated by the presence of electron-attracting substituents in the *o*- or *p*-positions [27]. More recent observations [28] suggest the formation of an intermediate copper complex of general structure 5.29, in which chlorine coordinates with copper. Coordination of chlorine with copper facilitates nucleophilic attack by the hydroxide ion at the carbon atom to which the chlorine is attached, leading to the formation of a *o,o*'-dihydroxyazo derivative.



## 5.6 PHYSICAL PROPERTIES OF METAL-COMPLEX DYES

### 5.6.1 Isomerism in metal-complex dyes

The fact that ligand systems are distributed in the space surrounding a central metal atom allows the possibility that metal complexes can form spatial isomers (stereoisomers). Metals of CN 4 may partake in either a tetrahedral or planar arrangement. With two symmetrical bidentate

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